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CHARACTERIZATION OF HOMOGENEITY OF GREEN ANODES THROUGH X-RAY TOMOGRAPHY AND IMAGE ANALYSIS

Kamran Azari[1,2], Behzad Majidi[1,2], Houshang Alamdari[1,2], Donald Ziegler[3], Mario Fafard[2]

[1] Department of Mining, Metallurgical and Materials Engineering, 1065 avenue de la Médecine
Laval University, Quebec, QC, G1V 0A6, Canada
[2] NSERC/Alcoa Industrial Research Chair MACE[3] and Aluminum Research Centre – REGAL
Laval University, Quebec, QC, G1V 0A6, Canada
[3] Alcoa Primary Metals, Alcoa Technical Center, 100 Technical Drive, Alcoa Center, PA, 15069-0001, USA

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Abstract

Homogeneity of green anode has a direct effect on final properties of baked carbon anodes. This work aimed to study the influence of mixing parameters on the homogeneity of laboratory-scale anodes. Anode pastes were made using different mixing times and temperatures and then underwent a compaction procedure. Homogeneity was characterized by the distribution of coke, pitch and porosity throughout the anodes as well as the variations in binder matrix thickness (fine coke + pitch). X-ray tomography was used as a non-destructive tool to evaluate the material distribution within the samples. The microscopic images of the green samples were analyzed to measure the mean thickness of binder matrix. The lowest variations in material distribution and the minimum thickness of binder matrix were obtained for the sample mixed at 178 °C for 10 minutes. The most homogeneous sample with the lowest binder matrix thickness had the maximum green and baked apparent density.

Introduction

Prebaked anodes are used in Hall-Héroult cells to produce aluminum. Calcined petroleum coke and coal-tar pitch are mixed to make a carbonaceous paste. The anode paste in then compacted and baked to achieve the required density and strength and also an improved electrical conductivity through carbonization of the pitch.

Mixing has an influence on the homogeneity of the paste and therefore that of the green anode. Better mixing can result in a more uniform distribution of coke aggregates in the binder matrix media that is a mixture of fine coke and pitch. Homogeneous distribution of binder matrix in the paste can reduce the amount of trapped air between the particles in the compacted paste. This can improve the anode properties by enhancing the anode density and reducing electrical resistivity and air permeability. Enhanced anode properties lead to improved energy efficiency in the electrolysis cell. There is also the possibility to reduce the pitch consumption with a homogeneous paste leading to lower level of volatiles and thus reducing the internal pressure and cracking rate during the anode baking [1].

A few researchers investigated the effect of mixing parameters on the anode quality. Belitskus [2] studied the effects of mixing time on the apparent density and electrical resistivity of green and baked bench scale anodes. He explained that there is an optimum mixing time for a given raw material and mixer. Mixing over the optimum time could decrease the apparent density and increase the electrical resistivity. Stokka [3] investigated the effects of mixing parameters on the volume of intra-particle pores. He found that at higher mixing temperatures a shorter mixing time was required to obtain a given pore volume. Clery [4] described that using an intensive mixer can improve the mixing effectiveness enhancing the consistency in the green apparent density (GAD). However, he did not describe how mixing variables influenced the paste and green anode properties. Azari et al. [5, 6] studied the influence of mixing time and temperature on the pore volume and pore size distribution in the paste and green anodes. They reported the optimum mixing variables to obtain the maximum green and baked apparent density.

A homogeneous paste can be obtained through an efficient mixing using sufficient mixing power and time, as well as proper mixing temperature. However, little has been published on the characterization of homogeneity of the paste and compacted anodes. Adams et al. [7] used X-ray tomography analysis to determine the density profile of carbon anodes and to identify the localized areas with inadequate amount of pitch.

The aim of this work was to determine the effect of mixing time and temperature on the homogeneity of green anodes. Non-destructive X-ray computerized tomography (CT) was used to determine the distribution of the constituents throughout the anodes. Thickness of binder matrix was also measured by image analysis.

Experimental procedures

A commercially available calcined petroleum coke with a real density of 2.057 g/cm^3 and a coal tar pitch were used as raw materials for making the laboratory scale anodes. Properties of coal pitch are indicated in Table 1. The coke was crushed and classified into the desired size fractions. A fine fraction with a Blaine number of 4000 was made using a ball mill. Table 2 shows the size distribution and proportions of coke particles used for making the anode paste. Seven combinations of mixing times and temperatures, indicated in Table 3, were used. Pitch and different size fractions of coke with the pitch/coke ratio of 16.2/100 were individually weighed, preheated at mixing temperatures, and added into the mixer to avoid variations in the composition of samples. The mixer was installed in the preheating oven to ensure a uniform temperature. The pastes were then compacted at 150 °C in a rigid cylindrical mold with an internal diameter of 68 mm. Compaction was performed to a maximum pressure of 60 MPa. The details for mixing and compaction procedures applied to the

pastes have been explained elsewhere [6]. Three samples for each set of mixing parameters were made.

Apparent density of the green anodes was calculated using geometrical volume and mass. Distribution of coke, pitch and porosity in the green anodes, that is an indication of mixing effectiveness, was determined by CT scan. CT is a non-destructive method that measures the intensity of X-ray after passing through the material. X-ray attenuation depends on the atomic number and bulk density of the material. Thus, X-ray intensity can be calibrated and associated with material density [8]. Adams et al. [7] and Picard et al. [9, 10] used this method to determine the apparent density of anodes. One sample for each set of mixing variables was scanned with a voxel resolution of 0.15 × 0.15 × 0.6 mm^3 using a Siemens Somatom Sensation 64. X-ray intensity expressed by CT numbers was recorded in Hounsfield unit (HU) and provided a 3D density map of the sample. CT images were constructed from CT numbers. Average and standard deviation of CT numbers were calculated. Maximum height of CT number profile (R_t) is the difference between the maximum and minimum CT numbers along the diameter of a slice. R_a is the average of the distance between the successive peaks and valleys of the profile. The R_t and R_a for CT number fluctuations were determined along the diameter of 10 slices from each green sample and the average was calculated. The 10 slices had similar positions in each green anode.

Table 1. Properties of coal tar pitch used as binder

Mettler softening point (°C)	Quinoline insoluble (%)	Viscosity (Pa.s)			
		158°C	168°C	178°C	188°C
109	15.5	4.08	3.15	1.12	0.66

Table 2. Size distribution of coke in the anode samples

Size range (US mesh)	Wt.%	Size range (US mesh)	Wt.%
-4+8	22	-50+100	8.8
-8+16	10	-100+200	10.8
-16+30	11.5	Fine	24.2
-30+50	12.7		

Table 3. Mixing time and temperature for making the pastes

Sample	1	2	3	4	5	6	7
Time	6	10	15	20	10	10	10
Temp. (°C)	178	178	178	178	158	168	188

A small part of each green sample with a surface area of 3-3.7 cm^2 was impregnated by a polishing resin under mechanical vacuum and polished. Optical microscopic images were processed with MATLAB image processing toolbox and the average thickness of binder matrix around the coke aggregates was determined. The variations of binder matrix thickness with mixing parameters were studied. The image processing approach can be summarized as follows:

- Grayscale micrographs of polished green anodes were taken with the magnification of 25X (Figure 1-a).
- Grayscale micrographs were converted to black and white (Figure 1-b).
- Two successive steps of dilation and erosion were performed and then holes within the coke regions were filled. The obtained black and white image was compared with the original image and dilation/erosion ratio was modified to minimize the possible movements of boundaries of the regions.
- All the coke particles (white regions in the image) with the equivalent diameter of less than 150 μm were considered as fine coke particles. All the fine particles were then converted to black to consider them inside a homogeneous binder matrix. By this step a black and white micrograph of green anode including coke aggregates (in white) and binder matrix (in black) was obtained (Figure 1-c).
- The iso-distance lines between the aggregates were then plotted in MATLAB. The image was scanned from the bottom to the top and the distances between the coke regions were recorded at each pixel row. Finally, the mean value of the binder matrix thickness and its distribution were obtained (Figure 1-d).

The top section of the samples was baked at a maximum temperature of 1130 °C for 12 hours. Water displacement method was used to determine the baked apparent density (BAD).

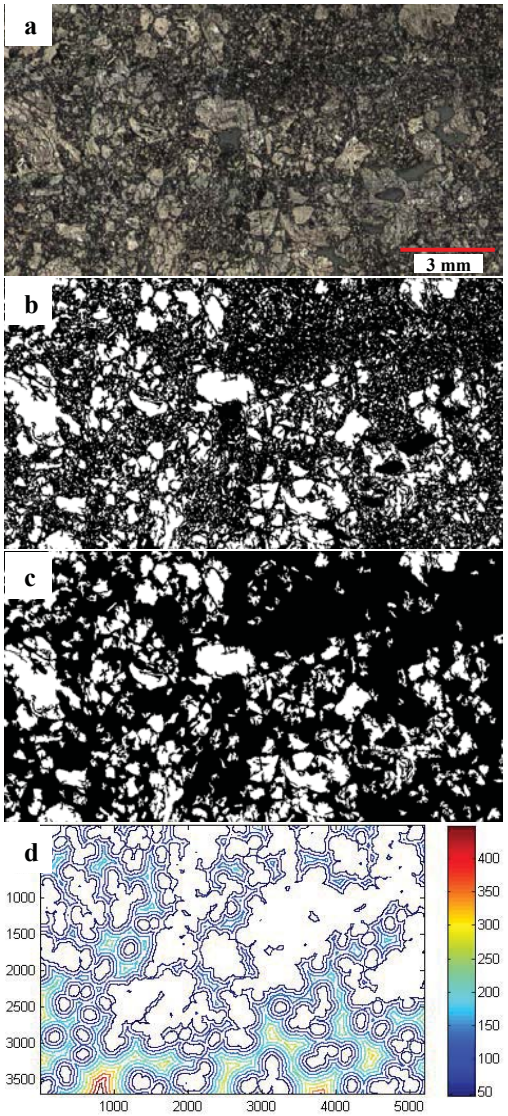


Figure 1. Image processing steps to determine the average thickness of binder matrix

Results and discussion

Figure 2 shows the variations in the average GAD and BAD as a function of mixing time and temperature. A meaningful variation was observed depending on the mixing variables. Increasing mixing time from 6 to 10 minutes at a mixing temperature of 178 °C led to an increase in the GAD, while mixing for longer than 10 minutes slightly reduced the green density. Increasing mixing temperature from 158 °C to 178 °C for a mixing time of 10 minutes enhanced the average GAD of the samples from 1.47 g/cm^3 to 1.51 g/cm^3. Further increase of mixing temperature to 188 °C reduced the green density to 1.49 g/cm^3 [6].

Variations in the apparent density of the baked sections in Figure 2 revealed a similar trend as that of green samples. At a mixing temperature of 178 °C, when mixing time was increased from 6 to 10 minutes, the average BAD was increased from 1.47 g/cm^3 to 1.52 g/cm^3. Longer mixing for 15 and 20 minutes decreased the density to 1.485 g/cm^3 and 1.489 g/cm^3, respectively. For a mixing time of 10 minutes, when mixing temperature was increased from 158 °C to 178 °C, the average BAD increased from 1.44 g/cm^3 to 1.52 g/cm^3. Mixing at 188 °C slightly reduced the baked density to 1.485 g/cm^3.

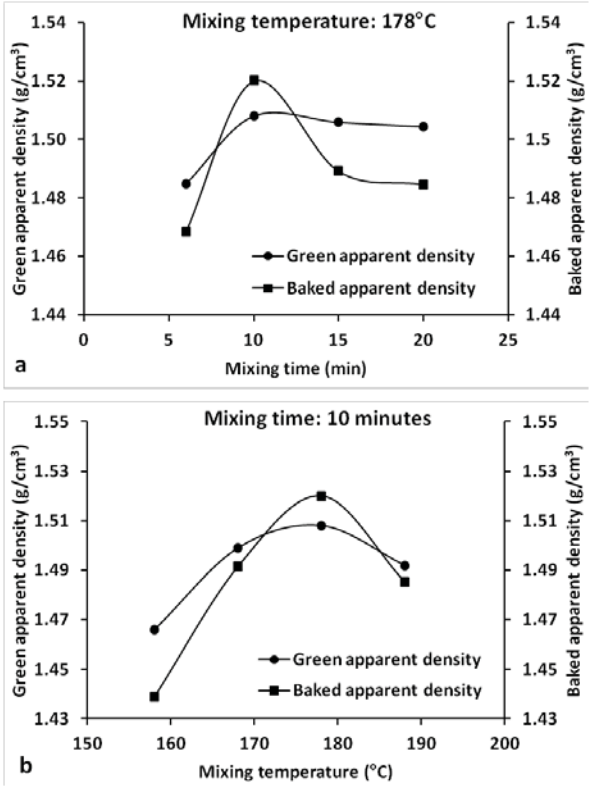


Figure 2. Variations in GAD and BAD as a function of mixing variables [6]

X-ray tomography was implemented to study the distribution of porosity in the green anodes. Figure 3 shows an example of CT images and CT number profiles along the diameter of two slices. The slices were located at the middle of the height of two green anodes made with different mixing temperatures. CT number fluctuations demonstrate the variations in the average density of the voxels. The anode mixed for 10 minutes at 178 °C was more homogeneous than that mixed for the same time but at 158 °C.

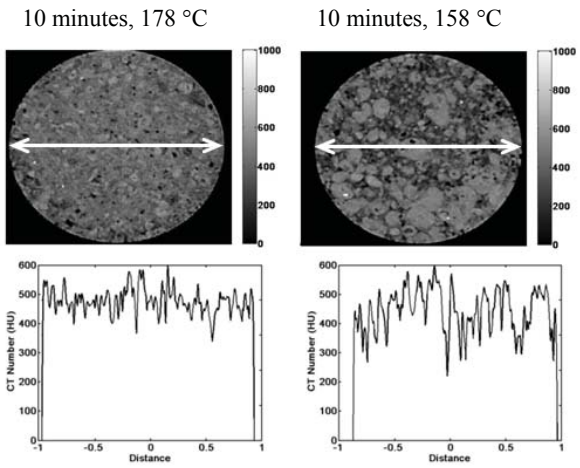


Figure 3. CT images and CT number profiles along the diameter of two slices of green samples made with different mixing temperatures of 158 °C and 178 °C

Figure 4.a shows the dependence of average and standard deviation of CT numbers on mixing time at a constant mixing temperature of 178 °C. Standard deviation of CT number decreased when mixing time was extended from 6 to 10 minutes but a meaningful variation was not observed beyond 10 minutes. It reveals that the anode mixed for 10 minutes or longer had a more homogeneous distribution of porosity, pitch and coke aggregates. In addition, for mixing times greater than 10 min, samples had the maximum of average CT number, indicating the maximum GAD. This is in a very good agreement with GAD results presented in Fig. 2 since the average CT number is directly related to the GAD.

Figure 4.b shows the standard deviation and average of CT numbers as a function of mixing temperature while a constant mixing time of 10 min was used. The standard deviation decreased significantly by increasing the mixing temperature from 158 °C to 178 °C, then it increased by further increase in mixing temperature. Mixing at 178 °C resulted in the maximum average of CT number that confirms the GAD results presented in Figure 2 assuming once again that GAD is directly related to the average CT number.

Figure 5 shows the variations in the R_t and R_a with mixing variables along the sample diameter (average for 10 slices). R_t and R_a are indicators for the distribution of the constituents (coke, pitch and porosity) in the green anodes. Smaller R_t and R_a values are associated with more homogeneous samples. The minimum fluctuations in density, i.e. minimum R_t and R_a, and therefore the best homogeneity were observed for the samples that were mixed at a minimum temperature of 178 °C for 10 minutes. These samples also resulted in the maximum GAD (Figure 2).

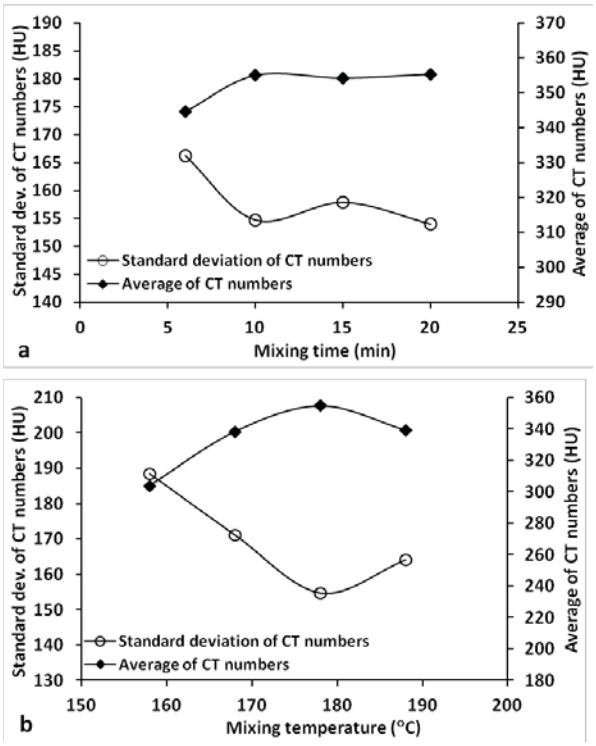


Figure 4. Standard deviation and average of CT numbers for green samples made with different mixing variables; (a) constant mixing temperature (178 °C), (b) constant mixing time (10 min) [6]

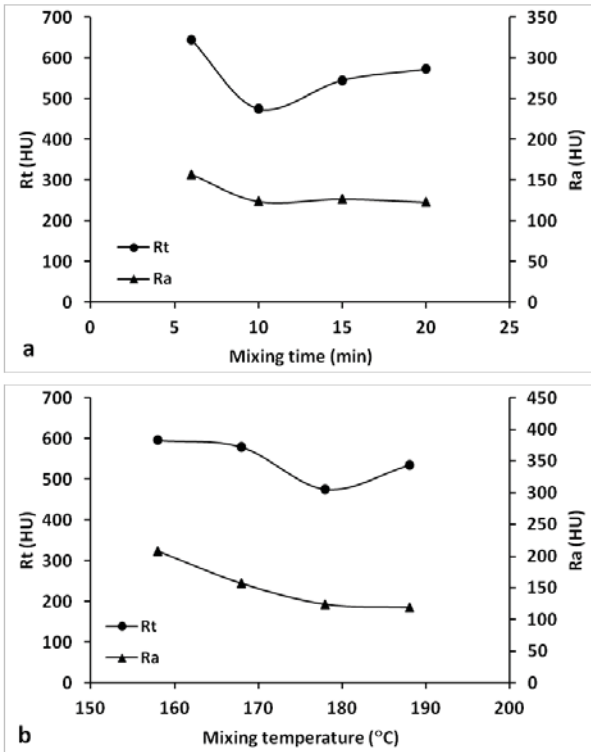


Figure 5. Variations in R_t and R_a with mixing parameters; (a) constant mixing temperature (178 °C), (b) constant mixing time (10 min)

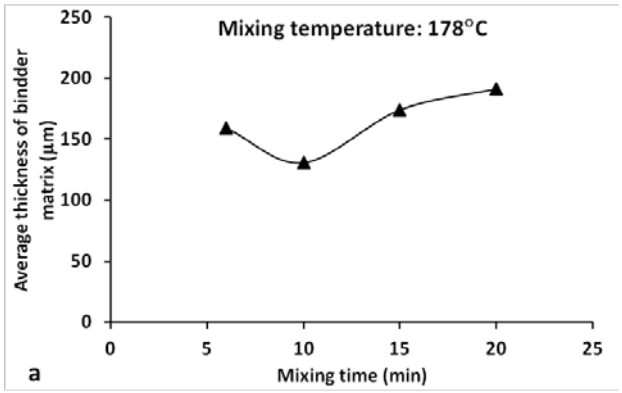
Average thickness of binder matrix is a measure of distance between the coke aggregates. It is expected that a more effective mixing result in lower variations for binder matrix thickness (particle distance) and therefore a higher GAD can be achieved. In previous works [5, 6] the higher GAD of samples that underwent a more effective mixing was attributed to microstructural aspects such as binder matrix thickness. In those works, microscopic images qualitatively showed that more effective mixing reduced the agglomeration of binder matrix and could result in lower variations and average for binder thickness. However, this parameter was not quantified in those works. Thickness of binder matrix was measured and provided in the present work. Figure 6 shows that thickness of binder matrix decreases with increasing mixing time to 10 minutes. It then increases for longer mixing times to values even above the initial one. This large increase is not in accordance with GAD of the samples where after 10 minutes of mixing GAD did not change significantly.

Figure 7 shows that by increasing mixing time from 6 to 10 minutes, the distribution of binder thickness moves towards smaller values. For instance, at 10 min, the fraction of binder thickness less than 100 μm increases at the expense of 100-200 μm. After 15 min of mixing, the thickness distribution becomes quite similar to that of 6 min. In other words, mixing over 10 minutes results in increasing the fraction of thicknesses in the range of 100-200 and 200-400 μm. Thus the average thickness increases.

Binder matrix thickness decreased with increasing mixing temperature from 158 °C to 178 °C (Figure 6.b). Mixing at 188 °C increased the binder thickness that is in agreement with GAD of the samples. Figure 8 demonstrates that increasing mixing temperature up to 178 °C led to a higher percentage of binder thickness in the range of <100 μm and 100-200 μm.

Figures 6-8 confirm the speculations that Azari et al. [5, 6] presented in their previous works.

Variations in the thickness of binder matrix were in accordance with those in the R_t, R_a, GAD and BAD. The mixing variables that resulted in a homogeneous green anode also led to the lowest thickness of binder matrix and the maximum apparent density. It was previously shown that lower thickness of binder, obtained by modifications in the paste formulation, resulted in a lower electrical resistivity [11, 12]. Homogeneity of the anode is therefore a determining parameter for anode quality. Thus, paste formulation and all the process variables that affect the homogeneity should be strongly taken into account in the anode production route.



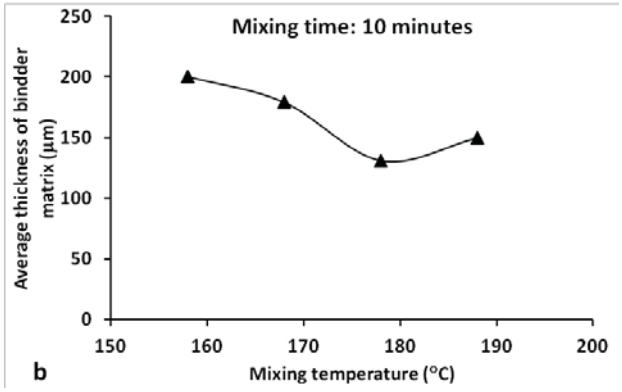


Figure 6. Variations of binder matrix thickness with mixing time and mixing temperature

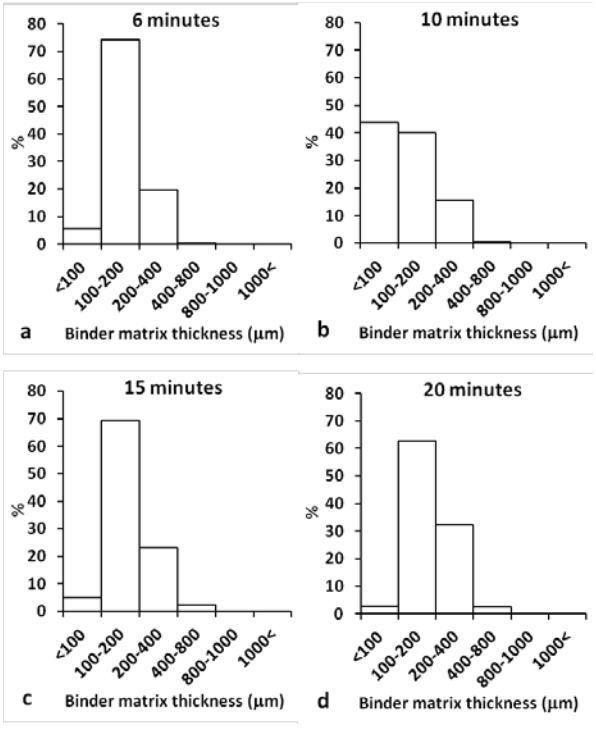


Figure 7. Distribution of binder matrix thickness for samples mixed at 178 °C for (a) 6 minutes; (b) 10 minutes; (c) 15 minutes; (d) 20 minutes

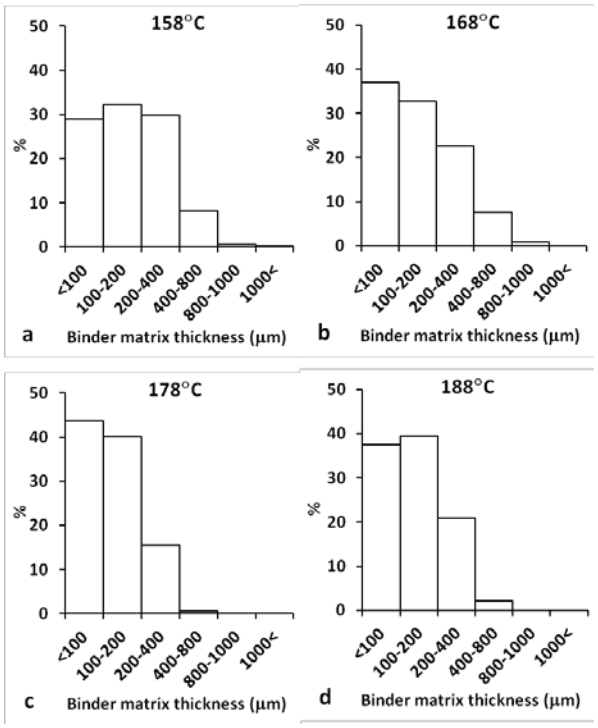


Figure 8. Distribution of binder matrix thickness for samples mixed for 10 minutes at (a) 158 °C; (b) 168 °C; (c) 178 °C; (d) 188 °C

X-ray tomography and image analysis are two complementary techniques. The information provided by tomography is an average for the materials included in a voxel and depends on the voxel resolution. In addition, coke and pitch have very close bulk densities and cannot be differentiated by tomography. Image analysis provides some additional information that is not revealed with tomography, e.g. thickness distribution of binder. However, care should be taken for dilation and erosion in an image to precisely distinguish different materials.

Conclusions

The present work showed that X-ray computerized tomography is a good method for characterizing homogeneity in green anodes. CT of carbon anodes revealed that the material is heterogeneous from the density point of view. The ability of image analysis to provide complementary information about the structure of the material was demonstrated. The homogeneity parameters correspond well with the binder matrix thickness and the measured apparent density. It is suggested that material homogeneity should be considered as an essential factor that has an influence on the anode properties and performance.

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